

DEVELOPMENT OF THE SULFURIC ACID CONTACT PROCESS

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There are still a few chamber type plants in existence for the production of sulfuric acid, but essentially all of the sulfuric acid produced today is made by the contact process. This process was discovered in 1831, but there was no real incentive for its development until about fifty years later. Even then it was almost another twenty years before production on a commercial scale was achieved. In the light of today's technology, it is difficult to appreciate the misconceptions that delayed the development of the process.

The early contact plants, producing about twenty tons per day in a single train, bear little resemblance to today's plant. A breakthrough about 1927 produced a flow sheet very similar to today's design and opened the way to the plants of today. The more recent changes in materials and design have permitted the increase in single train plant capacities from a maximum of about 100 tons per day to well over 2000 tons per day.

For most of the early history, we are indebted to two books. They are "Manufacture of Sulfuric Acid (Contact Process)" by F. D. Miles, published in 1925 by Gurney and Jackson, and "Sulfuric Acid Manufacture" by Andrew M. Fairlie, published in 1936 by Reinhold Publishing Corporation.

Early History

One hundred fifty years ago people were very content to produce the sulfuric acid they needed by the chamber process. Sulfur dioxide from any of several sources reacted with oxygen in the air to form sulfur trioxide which combined with water vapor in the air to form sulfuric acid. The oxidation rate was slow, but it was improved by the introduction of oxides of nitrogen into the gas stream. An intermediate product, nitrososulfuric acid, was formed which decomposed on dilution to regenerate the nitrogen oxides. The heats of reaction were high and the process was carried out in a series of large air cooled lead chambers to provide sufficient cooling surface. The maximum product acid concentration was 60° Baume (77.67% H_2SO_4), but this could be concentrated to 66° Baume (93.19% H_2SO_4) by boiling if this higher strength was required.

In 1831 Peregrine Phillips, a vinegar manufacturer of Bristol, England, disclosed a new process in his British Patent No. 6096. He described the instantaneous union of sulfur dioxide with atmospheric oxygen when passing the mixture over platinum which had been heated to a strong yellow heat. He said further that the sulfur trioxide which is formed will be rapidly absorbed when it comes in contact with water to form sulfuric acid.

In spite of the obvious advantages of the contact process over the chamber plants, the commercial development of the process was extremely slow. The chemical technology of the time, especially with regard to catalytic reactions, was very meager. The first observation of a "contact" reaction seems to have been made by Edmund Davy in 1817. He noted that heated platinum wire introduced into a mixture of oxygen or air with hydrogen, carbon monoxide, or ethylene became hotter and finally glowed with rapid combustion of the mixture.

Misconceptions

During the next forty years, there was some interest in duplicating Phillips' work and in looking for other catalysts, but there were no meaningful developments. Other catalytic effects had been observed and there was some thought that substances capable of this "contact" action owed their properties to their porosity. The gases were thought to be condensed in the pores and, with the resulting smaller volumes, the molecules were in closer "contact" so they could react more easily.

In 1852 Wohler and Mahle discovered that oxide of copper or chromium at a low red heat caused formation of thick fumes of sulfur trioxide when the constituent gases were passed over it. They also demonstrated that oxide of iron or oxide of copper is capable of either reduction or oxidation under the conditions of the experiment, depending on whether dioxide or trioxide is present in excess. This should have generated a recognition of equilibrium conditions with temperatures and partial pressures of reactants, but apparently it did not.

In 1875 Clemens Winkler, professor in the School of Mining at Freiberg published a paper reporting his work. His experiments were obviously faulty and his conclusions contradicted the principles of mass action which had been enunciated eight years earlier by Guldberg and Waage. In spite of this, his paper was widely accepted and it influenced general opinion for many years. Based on his experiments, he stated that "the action of platinised asbestos and of all other contact substances is diminished in the same measure as the dilution of the sulfur dioxide by other indifferent gases is increased. Even sulfur dioxide and oxygen will naturally remain indifferent and act as diluents in so far as they are present in other than the stoichiometric ratio necessary for acid formation. That is, in so far as one gas or another is in excess." His paper did not report the ratio of oxygen to sulfur dioxide in his tests, but he reported 73.3% conversion when operating

with pure sulfur dioxide and oxygen. If the oxygen was replaced by oxygen and air, the conversion dropped to 47.4%. When using a gas resulting from burning sulfur in air containing four to five percent sulfur dioxide, the conversion dropped to 11.5%.

This faulty information came at a most unfortunate time and undoubtedly delayed the commercial implementation of the contact process. At the time of Phillips' patent, there was no particular need for a process which could produce fuming acid. The small quantities that were required were produced by fortifying concentrated chamber acid with SO_3 made by decomposition of "copperas-slate".

The Incentive

Shortly before the publication of Winkler's misleading paper, the synthetic production of alizarine and other dye stuffs was developed. Most of these required the preparation of sulfonic acids in intermediate stages and the demand for fuming sulfuric acid rose abruptly. The existing fortification plants in Bohemia were inadequate to meet the demand and various approaches to the new contact process were tried.

Early Plants

The first commercial plants were producing fuming acid, about 40% oleum, by 1880. Both Winkler in Germany and Squire and Messel in England developed commercial plants based on decomposing weaker sulfuric acid by heat to form SO_2 , O_2 , and water vapor. The water was condensed and the SO_2 and O_2 , in essentially stoichiometric ratio, were passed over platinised pumice. The SO_3 produced was condensed as fuming acid. These plants produced several tons per week of trioxide.

The decomposition of acid to produce sulfur dioxide was short lived because of the corrosion problems. It was still felt that rich SO_2

gas with a minimum of dilution was a necessity. Squire developed a process in which sulfur was burned in air and the resulting SO_2 was absorbed in water under a pressure of 4 atmospheres. The SO_2 was expelled by steam, mixed with the theoretical quantity of air, and passed over heated platinised asbestos. The trioxide formed was absorbed in concentrated acid to produce 40% oleum. The tail gas was recycled to obtain an overall yield of 90%. The daily production was 30 cwt of trioxide, which is equivalent to 2 tons of acid per day.

During this period and until nearly the end of the century, Winkler's ideas of maintaining stoichiometric ratios of oxygen and sulfur dioxide with minimum dilution still affected the general approach to the contact process. In all cases, the catalytic apparatus was externally heated and there was apparently no recognition of the fact that overall conversion efficiency could be improved at lower operating temperatures or that the heat of reaction could be used to preheat the feed gas stream.

The final blow to Winkler's ideas was Knietzsch's lecture in 1901 before the German Chemical Society. In it, he described some of the work that had been carried out in the laboratory and the plant of the Badische Company. Knietzsch and his collaborators had made extensive studies of operating conditions with platinum and other catalysts, had determined physical properties of fuming acid and sulfur trioxide and had found solutions to the technical problems that had plagued the use of pyrite burner gases. They found that contact vessels required cooling rather than heating, and they had generally made the contact process so successful that it could not only produce fuming acid cheaply, but it could compete with the established chamber process in the production of ordinary concentrated acid.

One of the problems had been that the contact mass gradually lost its activity even though the burner gases had been passed through several

stages of purification - cooled in long pipes, washed with acid, and filtered through coke and asbestos. They found that minute traces of certain elements, such as arsenic, that were carried through to the contact mass in the sulfuric acid mist were causing the loss of activity. This and other work made it obvious that gas purification is a most important section of a contact sulfuric acid plant.

Successful Plants

Successful contact plants were developed by several groups during the same period just before the turn of the century. There were differences in the form of the catalyst, in the manner of heating and cooling the gases, and in the type of gas purification, but the differences were no greater than those between different contractors today.

There was, however, one unique one - the forerunner of today's double absorption, or double catalysis, process. This was the Mannheim process patented in 1898 and 1899. In this process, the first stage of conversion was carried out with a ferric oxide catalyst. This was followed by absorption of the SO_3 produced, then by a second conversion stage using platinum catalyst, and by a final absorption. This scheme had an obvious advantage in conversion efficiency, but its use was short lived. Heat recovery in those early days was inefficient, and the double absorption scheme required additional fuel firing as well as additional absorption equipment.

The acid plants built in the early part of this century were unbelievably complex and large for their production capacity in comparison to the present-day design. The first experimental contact plant in the U.S. was built in 1898 in New Jersey by Badische. By the time Miles' book was published in 1925, he reported that there were 48 contact plants in the United States.

As an example of the type of plant built here during that early period Miles gave us a good description of a plant built in 1918 for the U.S. Government at Nitro, West Virginia. It was a wartime rush job and did not include regenerative converters but it did include more scrubbing apparatus that would normally be included to permit possible operation with pyrite instead of sulfur. The acid was required for the production of 300 tons per day of smokeless powder.

The plant consisted of seven units of four systems each, or a total of 28 individual trains. Each train had a capacity of 16 tons per day of sulfur trioxide, or about 20 tons of acid per day. The total building floor space required was about 300,000 sq. ft., or nearly seven acres, for a total acid production of about 550 tons per day. The trains were laid out in almost straight lines and one group of four trains required a plot area about 190 ft. wide by about 425 ft. long.

The following description applies to a single train producing nearly 20 tons per day of acid. Lump sulfur was delivered by wheelbarrow from a concrete storage bin to the feed hopper of a Glens Falls burner. This was a kiln 4 ft. diameter by 16 ft. long which rotated slowly to expose the sulfur-wetted walls to the combustion air stream. This air was induced through the burner by the blower downstream of the gas cleaning and drying system. The gas passed through a cast iron combustion chamber to complete the combustion and then through a bank of vertical cast iron pipes where it was partially cooled by air. The gas then went to a hot gas scrubber, a water sprayed lead tube gas cooler, and a cool gas scrubber. Each of these scrubbers was 8 ft. square by 20 ft. high of acid brick lined lead construction with quartz packing. The lead tube gas cooler consisted of 750 lineal ft. of 6" lead pipe arranged in 16 runs 45 ft. long. The two towers acted as gas cooler and predryer. In the first tower, the hot gas was cooled by concentrating the acid returned from the second tower. Water was condensed from the gas in the water-cooled lead tube unit and more water was removed from

the gas in the second scrubber by the cooled concentrated acid. The weak acid was then reconcentrated in the first tower.

The pre-dried gas passed to the coke filter, which was a lead box 30 ft. long by 12 ft. wide by 10 ft. high reinforced with timber. The filter was packed with coarse coke on the bottom and 3 to 4 ft. of fine coke on top and the gas passed from the bottom at one end to the top at the other end. Next in order were the mineral wool filters of which each train had five units in parallel. These were shallow cast iron vessels 6 ft. in diameter, each with two lead screen filter supports. On each screen was a 1" layer of cotton fiber and an 8" layer of mineral wool. The gas passed downward through the filter layers and then went to the bottom of the quartz packed drying tower over which 98% acid was sprayed. Before the dry gas went to the blower, it passed through a quartz packed steel tower to eliminate any carryover of spray from the drying tower.

The blower was motor driven with a capacity of 3000 cfm. It provided sufficient suction to draw the air into the sulfur burner and through the entire gas cleaning section and sufficient pressure to deliver the gas through the balance of the plant. Information was not available for this particular plant, but for this type of plant, the blower suction was on the order of 1 to 5 in. water gauge and the discharge was 10 to 30 in. water gauge.

In this particular plant, there was no provision for recovery of the heat from the converted gas. The gas leaving the blower was indirectly heated by gas burners to 400°C in cast iron U pipes in two heating chambers. The gas then passed to four converters in parallel which were 5 ft. diameter by about 10 ft. high, each with five layers of catalyst. The catalyst was 1/4 to 3/4 in. magnesium sulfate which had been platinised after sizing. The percentage of platinum varied from 0.15 to 0.30% with the richer mass in the first pass. The gas entering the converter normally contained about 5.5% SO₂.

The gas leaving the converter at 500° to 550°C was first cooled in cast iron pipe and then in water-sprayed steel pipe. The cooled gas passed through two absorbers in series and then through a spray catcher before going to the stack. The first absorber was a steel shell 5 ft. diameter by 11 ft. high lined with acid proof brick and packed with quartz. Acid from the final absorber was advanced batchwise to the first absorber over which it was sprayed until the concentration reached 27% oleum. A second similar absorber was added later to produce 40% oleum. In that case, the first absorber produced 16% oleum.

The final absorber was similar to the first but larger, 7 ft. diameter by 15 ft. high. The circulating acid was maintained at about 99% by feeding recovered spent acid from the nitration plant and weak acid from the gas cleaning section of the acid plant.

This plant installation, although larger than most, was generally typical of the type of equipment and size of the individual trains which make up the plant. It was, however, a wartime emergency installation and it was dismantled some time prior to 1925.

A sulfuric acid plant installation list of about 1920 showed that there were acid plants at 228 locations in the United States and that there were contact type plants at 53 of these locations. The balance of the plants were of the chamber type.

Design Breakthrough

According to Fairlie, a major simplification of sulfur burning acid plants was introduced by Chemico in 1927. The novelty included pre-drying of the combustion air and pre-melting of the sulfur so that it could be spray burned in a furnace operating under pressure. These features eliminated the necessity for an extensive gas cleaning system

and required only a hot gas filter to remove sulfur ash from the gas stream. With pre-dried air and pre-melted sulfur, there was practically no moisture in the gas stream and no acid mist to be removed. With the elimination of the need for wet scrubbing of the combustion gas, it remained hot and did not require preheating before entering the converter. Actually, some cooling of the gas was required and a waste heat boiler was provided after the sulfur furnace. The steam production in this boiler was increased by the use of the Selden converter in which the inlet gas was preheated by the heat of reaction in a built-in heat exchanger.

The first units of this type were built for Standard Wholesale Phosphate and Acid Works in Baltimore, Maryland and for American Cyanamid Co. in Warners, New Jersey. The largest single train plant with Selden converters was normally 120 tons per day of H_2SO_4 , and Fairlie provided a fairly detailed description of this size plant as built about 1928 to 1930. It is summarized in the following paragraphs.

The entire acid plant, with the exception of the acid towers, was normally installed in a building 60 ft. wide by 100 ft. long by 40 ft. high to the roof trusses with an overhead crane for repair work.

The brick lined below grade concrete sulfur melting pit was generally located next to the sulfur furnace. For the 120 ton per day plant, it was approximately 30 ft. long by 8 ft. 8 in. wide by 3 ft. 6 in. deep with five transverse steam coils. Steam was supplied to the coils at 75 psig and solid sulfur was charged to the pit by buggy at regular intervals. A vertical submerged turbine-driven sulfur pump installed in a partitioned section with an underflow opening at one end of the pit delivered the molten sulfur at 275°F through a steam jacketed sulfur line to a specially designed jacketed spray burner installed in the sulfur furnace.

The two air drying towers were located in a line with the three absorption towers outside of the building at the opposite end from the sulfur melter and furnace. All five of the towers were 11 ft. diameter by 28 ft. high steel shells lined with 4 in. of acid brick. The first drying tower, which was downdraft, was packed with 14 ft. of 3" spiral rings, stacked and staggered, plus 3 ft. of dumped 3" rings on top over which 93% acid was circulated. The second drying tower was updraft and was packed with 17 ft. of dumped 3" spiral rings. It operated dry and served only to remove entrained acid droplets from the dried air. The air went to a 220 hp turboblower which delivered it at 45" W.G. pressure to the sulfur furnace.

The sulfur furnace was a horizontal steel vessel 11 ft. diameter by 30 ft. long with 9 in. of fire brick and 4-1/2 in. of insulating fire brick lining. There were two fire brick baffles spaced several feet apart with over and under gas openings. The normal furnace operating temperature was 700°C with a 7% SO₂ gas being produced. The hot furnace gas flowed down through a "rock filter" where fly ash from the sulfur was removed. This was a vertical steel shell 10 ft. diameter by 18 ft. high lined with 4-1/2 in. of insulating fire brick and packed with about 7 ft. of 3" and 4" quartz lumps. This was followed by a waste heat boiler operating at 150 psig in which the gas was cooled to about 300°C.

The gas next went to the Selden converter. In the 120 ton per day plant, there were three 40 ton per day converters in parallel. These were cast iron vessels 10 ft. 6 in. diameter by 16 ft. high with two stages of conversion and two sets of built-in heat exchangers. The gas entered at the side of the bottom section and passed upward through a tube sheet and tubes. The tubes were fitted with cast iron caps of larger diameter that extended almost back to the tube sheet so that the gas reversed direction. In the space between the capped tubes, there was a 3" layer of quartz pebbles on the tube sheet and above

that about 3 ft. of 3/16" pill-shaped vanadium catalyst pellets. The heat of reaction in the catalyst bed preheated the incoming gas as it passed through the many parallel tubes and caps imbedded in the catalyst bed. This built-in exchanger also cooled the gas in the upper portion of the first catalyst bed so that the conversion reaction could proceed further than it could if the bed were not cooled. The second catalyst bed was supported on a screen on a perforated plate. It was cooled by a similar set of double tubes extending down from the top of the vessel with air blowing through the tubes. This upper bank of tubes was eliminated in later plants, and additional cooling was provided by extending the lower set of tubes above the catalyst in the first bed.

With this two-stage converter and with cooling carried out within each of the two catalyst layers, conversions of more than 97% were reported for operation with a 7% SO₂ gas from sulfur burning and with a catalyst loading of about 190 liters per daily short ton of acid produced. When cooling of the upper bed was eliminated, the conversion efficiency was reported to have dropped by about 0.5%.

The gas leaving the converters was cooled to about 105°C before going to the absorbers. The cooling was accomplished in an air-cooled carbon steel shell and tube exchanger in which the gas flowed down through the tubes. In some cases, this low temperature resulted in acid mist in the stack gas and the cooling had to be limited to 140° or 150°C.

The absorbers were the same design as the first drying tower described previously. There were three towers in series, with the gas flowing upward in all three. The first two were absorbers with 98% acid recirculated over them and the third was a dry spray catcher the same as the second drying tower. The acid was circulated over the first absorber at 80°C and over the second at about 45°C. The acid flowed by gravity from the towers through cascade type cast iron pipe coolers.

to the pump tanks. These were horizontal cylindrical steel tanks with acid brick lining and with Rumsey vertical submerged pumps. In the smaller plants, the acid reservoir was in the base of the tower and horizontal suction lift LaBour pumps were mounted on a platform above the acid coolers.

At about the same time that Chemico was building the above plants, Leonard Construction was building a somewhat similar plant for Merrimac Chemical at Everett, Massachusetts. This was a plant to produce 75 tons per day of acid using molten sulfur and pre-dried air. The solid sulfur was melted with steam coils in a similar below grade pit. The sulfur was elevated to the vertical sulfur furnace by a submerged deep well type of plunger pump driven through a variable speed reducer.

The air drying tower was a rectangular lead tower 8 ft. 6 in. square by 22 ft. high supported by a steel frame. The tower was brick lined and packed with glass plates on edge supported on brick courses. The dried air went to a high pressure blower with a capacity of 5000 cfm. At full plant rating, the required blower discharge pressure was 40" W.G.

The sulfur furnace was a vertical steel cylinder 13 ft. diameter by 25 ft. high divided into two compartments by a fire brick arch. Molten sulfur, admitted at the top, fell on a splash plate on top of a checkerwork brick pyramid built on the brick arch. Air was delivered under pressure at two points, one near the sulfur feed and the other at the level of the arch. The sulfur burned as it flowed down through the pyramid. The combustion gas and any unburned sulfur passed down through the arch where the sulfur was exposed on additional brick checkerwork for more complete combustion. This plant is reported to have operated with a 9% SO_2 gas and a vanadium catalyst loading of only 113 liters per ton, with a conversion efficiency of about 95%. The plant did not have a waste heat boiler, but cooling of the SO_2 gas

leaving the furnace and the SO_3 gas going to the absorber was accomplished by preheating air for the boilers of the power house next door.

A gas filter was installed ahead of the converter. It was 11 ft. diameter with a 14" layer of catalyst pellets, without the vanadium, as the filter material. Two converters, operated in series, were cast iron shells 11 ft. diameter. There were two beds of catalyst in the first converter, each about 7-1/2 in. deep, supported on woven wire shelves. The gas was heated in the first converter from about 405°C to 580°C and was cooled to about 405°C before entering the second converter. This had three catalyst beds, each about 12-1/2 in. deep, and the gas left at about 460°F. The above catalyst depths indicate a catalyst loading of about 160 liters per ton based on 75 tons per day operation, as compared to the 113 liters per ton indicated above.

Shell and tube gas to gas exchangers were used to cool the gas leaving each of the converters and to preheat the SO_2 going to the first converter. This cooled the SO_3 to 275°C and it was further cooled in an air-cooled unit as indicated earlier. The SO_3 was absorbed in a conventional acid brick lined steel tower packed with ceramic rings and French pebbles.

This plant had an unusual feature for its time that anticipated the EPA. It had a device which automatically stopped the blower and the sulfur pump in case of any interruption of the flow of acid to the absorption tower.

Fifty Years Later

The flow diagram for a sulfur burning sulfuric acid plant today still bears a close resemblance to that of fifty years ago. Molten sulfur is spray burned in pre-dried air. The gas is cooled in a boiler

before going to the converter, and the converted SO_2 gas is absorbed in a packed tower. The flow scheme remains the same but there have been changes in nearly every aspect of the plant.

Capacity. The maximum capacity of a single train plant has increased about twenty-five fold. With today's technology, a 3000 ton per day plant is well within current design capabilities. The increase is partly the result of larger equipment. It is also the result of experience which proved that residence times could safely be reduced and gas velocities increased.

Sulfur. Originally, lump Frasch sulfur was shipped and stored in the open. After it was melted some of the contaminants settled in the melting pit, some were skimmed off, and the rest were stopped either in the hot gas filter or in the catalyst. Sulfur filters were popular for a while for use instead of gas filters. Finally, filtered molten sulfur shipments became available from strategically located terminals, and most plants today have no sulfur melting facilities or sulfur filters.

Heat Recovery. Most modern sulfur burning plants recover more heat as steam and at a higher pressure than the early plants. Boilers in the early plants usually operated in the 150 to 250 psig range, compared to today's 450 to 600 psig range, with one or two plants operating at over 800 psig. Today's higher pressure, along with superheat, provides more potential energy per unit of heat recovered than the early low pressure plants. In most cases, however, we are still a long way from utilizing the full potential.

Conversion. There has been some improvement in catalyst efficiency, but it is still the vanadium pentoxide that was introduced in the twenties. Converter design has been improved with more stages and better temperature control. Conversion efficiency has been improved

from a nominal 98% to more than 99.7% by the reintroduction of the double absorption process, which first appeared sometime before 1900. Tail gas emissions are also reduced by SO₂ absorption as sodium or ammonium salts, with recycle of the recovered SO₂ to the acid plant.

Acid Towers. A change in the type of packing from 3" spiral rings to 3" saddles permitted a tripling of the gas velocity in the tower with a reduction in pressure drop. Improvements have been made in lining materials and acid-proof mortars, as well as in the techniques for their installation. Mist and entrainment separators have been developed to take the place of the early dry spray catcher towers or the later use of a layer of dry packing near the top of the tower.

Acid Coolers. There has been a considerable change from the early cascade type of cooler using banks of 6" cast iron pipe. It was changed almost entirely in the 40's to the well-known cast iron AX sections. These were more efficient and permitted a reduction in the size of the acid cooler pit. In the 70's, several new types of coolers appeared on the market in this country. These include stainless steel shell and tube units with and without anodic passivation, tanks with teflon tube bundles for cooling water, air-cooled stainless steel or cast iron units and plate type coolers. These have met with varying degrees of acceptance as well as of success. All of the newer units have eliminated the traditional acid cooler pit with its steam plume in cold weather but most of them require cooling water and therefore probably a water cooling tower.

Materials of Construction. In sulfur burning plants, there is very little change. The plants are still primarily steel and cast iron. The one area that has changed is valves. The 316 and Alloy 20 valves have replaced the hard lead valves and cast iron plug cocks that were the standard in the old plants.

In the early wet gas plants, lead was the only material available for gas ducts, tower linings, and weak acid piping. This has been almost entirely supplanted today by plastics and stainless steel.

Pressure Plants. Plant operation with higher pressure has attracted attention at various times and a commercial plant was built. The reduction in equipment size and the improved conversion efficiency under pressure are attractive, but the overall economic advantage is still under question. Papers to be presented by Ugin Kuhlmann and Chemetics International, Ltd. at the Philadelphia meeting next month should shed more light on this subject.

Summary. From the strictly process point of view, it is disappointing to realize that there has been so little improvement in the basic process in the last fifty years. Hopefully, this is proof of its fundamental soundness.

Today's sulfuric acid plant is more compact, more reliable, more highly instrumented, and much more expensive than its predecessors.

